Specific Heats of Ammonium, Potassium, and Sodium Chloroiridates

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The specific heats of ammonium, potassium, and sodium chloroiridate have been measured between 1.5°K and 20°K; anomalies of the λ-type were found at 2.15, 3.05, and 3.95°K for the ammonium, potassium, and sodium salts, respectively. These results confirm some conclusions drawn from magnetic susceptibility values. The difficulties involved in the correct analysis of this type of specific heat measurement are discussed.

EXTENSIVE investigations of the magnetic properties of chloroiridate salts have been made in this Laboratory during the past few years.[1–3] Part of the program was to measure the specific heats of these salts. The paramagnetic resonance work on low concentrations of iridium ions present in ammonium chloroplatinate indicated that there might be antiferromagnetic transitions in the liquid helium temperature range in the chloroiridate salts. Antiferromagnetic transitions are accompanied by a λ-type anomaly in the specific heat and the presence of such an anomaly provides the most distinct confirmation that there is such a transition. Accordingly, we have made specific heat measurements on the face-centered cubic salts, $(NH_4)_2IrCl_6$ and K_2IrCl_6, and on the triclinic salt, $Na_2IrCl_6 \cdot 6H_2O$. Anomalies of the λ-type were found at 2.15°K, 3.05°K, and 3.95°K in the specific heats of the ammonium, potassium, and sodium salts, respectively, as are shown in the figure. The measurements were made in the temperature range 1.5°K to 20°K.

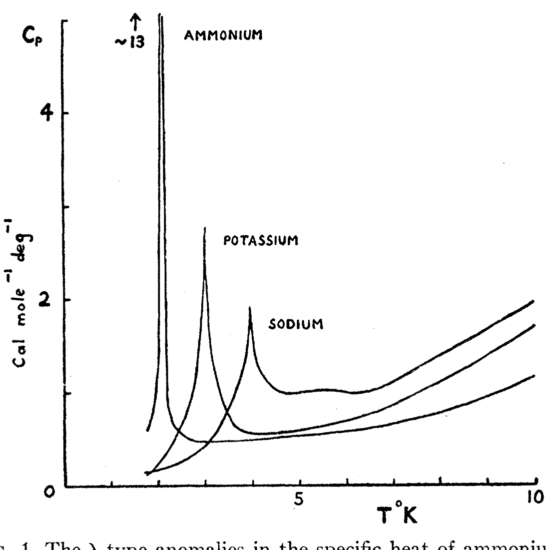

FIG. 1. The λ-type anomalies in the specific heat of ammonium, potassium, and sodium chloroiridates.

The transition temperatures can be defined as the temperature of the peaks in the specific heat curves. It was found that these temperatures for the ammonium and the potassium chloroiridates correspond to those at which the susceptibilities show the greatest rate of decrease with temperature.[3]

The salts were prepared by Johnson Matthey of London and classified as high-purity material. They were all fine powders and preliminary experiments on the ammonium salt showed that it could be cooled through the anomaly only with difficulty. This problem was overcome by using a calorimeter containing a set of eight radial fins made of thin copper sheet.

The anomalous entropy was found to be of the order of $R\ln 2$ for each salt as was to be expected for a system with spin $\frac{1}{2}$. This approximate result was found by roughly fitting those parts of the specific heat curves lying well above the peaks to equations of the form

$$C = C_{\text{lattice}} + C_{\text{anomaly}},$$

assuming that

$$C_{\text{lattice}} = AT^3,$$

and

$$C_{\text{anomaly}} = b/T^2.$$

In fact, the experimental results did not fit closely a curve of this form, which is not surprising in view of these assumptions. For the anomalous specific heat to vary as $1/T^2$, the temperature must be well above the transition temperature; but here the lattice is unlikely to vary as T^3.

Measurements on the diamagnetic ammonium, potassium, and sodium chloroplatinates are, however, to be made in the near future, since the specific heats of these salts should represent very closely the corresponding lattice terms of the chloroiridates and enable the anomalous contributions to be evaluated more accurately.

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[3] Cooke, Lazenby, McKim, Owen, and Wolf, Proc. Roy. Soc. (London) (to be published).